It is evident that a definite compound is secured by this method even though not absolutely pure. Making the comparison first on the water-free basis we have:

	A.		B.		C.		Average.	$Zr_3O_5.CrO_4$.
% CrO_3....	21.87	21.48	20.79	20.55	20.84	20.91	21.08	21.16
% ZrO_2....	77.75	78.09	79.21	79.45	79.15	79.09	78.79	78.84

A comparison on the analysis direct would be:

	A.		B.		C.		Average.	$2ZrO(OH)_2$.-$ZrO.CrO_4.8H_2O$.
CrO_3.....	15.87	15.58	14.91	14.86	15.09	15.11	15.40	15.35
ZrO_2.....	56.40	56.64	56.82	57.44	57.34	57.15	56.97	58.54
H_2O.....	27.52	27.40	28.00	28.40	27.09	27.35	27.63	27.64

Close accord in results was not to be expected when air-dried samples were used for analysis. The deduction seems justified, however, that when chromium trioxide and zirconium hydroxide are mixed in varying proportions in the presence of an abundance of water there is a tendency to form the insoluble basic chromate $2ZrO(OH)_2.ZrO.CrO_4.8H_2O$, and that the favoring conditions are increase of temperature and excess of water. This precipitation of basic compounds of zirconium under these conditions, especially by boiling, is well known in cases of other acid radicals especially organic.

Perhaps for the basic chromate the following steps in the reaction may be indicated: First, the formation of the normal chromate $Zr(CrO_4)_2$, which is immediately hydrolyzed to $ZrOCrO_4$. Some of the $Zr(OH)_4$ is also partially dehydrated to $ZrO(OH)_2$ and the insoluble combination of these two substances is precipitated as $2ZrO(OH)_2.ZrO\ CrO_4.8H_2O$.

Summary.

1. The results obtained would seem to controvert those of Haber.

2. A definite basic zirconium chromate is obtained on diluting and boiling solutions of zirconium hydroxide in chromic acid, to which the formula $2ZrO(OH)_2.ZrO.CrO_4.8H_2O$ may be assigned.

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[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORY.]

THE QUANTITATIVE ANALYSIS OF SMALL QUANTITIES OF GASES.

BY H. M. RYDER.

Received September 3, 1918.

In some work on the study of gases in metals it was considered desirable to heat the metal in a cold envelope in order to eliminate as far as possible all sources of error. The most convenient method of doing this was by the passage of an electric current through the metal specimen itself. This and other conditions made necessary the use of small quantities of metal, which in turn meant the analysis of very small quantities of gases. This analysis had to be accurate to within 5% of the whole, or 30% or 40% of any constituent whose total quantity was less than this amount, if the work was to be valuable.

As quantities of gas as small as a few cu. mm. at atmospheric pressure had to be analyzed if the conditions accepted for the problem were to be fulfilled, ordinary absorption methods of analysis were not possible, since even an absorption apparatus of very small dimensions could not take care of so small a quantity of gas. The method described in this paper was therefore developed to provide for the accurate analysis of such small quantities of gas as should be removed from the metals in the course of their study.[1]

In general, the method provided for the separation and measurement of water vapor and carbon dioxide, using liquid air and solid carbon-dioxide, the addition of oxygen or carbon monoxide, in excess, to the remaining gases, the combustion of this mixture, the separation and measurement of the products of combustion, and the adding of carbon monoxide or oxygen to the residue, and the repeating of the combustion. The measurement of necessary pressures in a system of known volume, at different stages of the process provides data for the accurate calculation of the analysis.

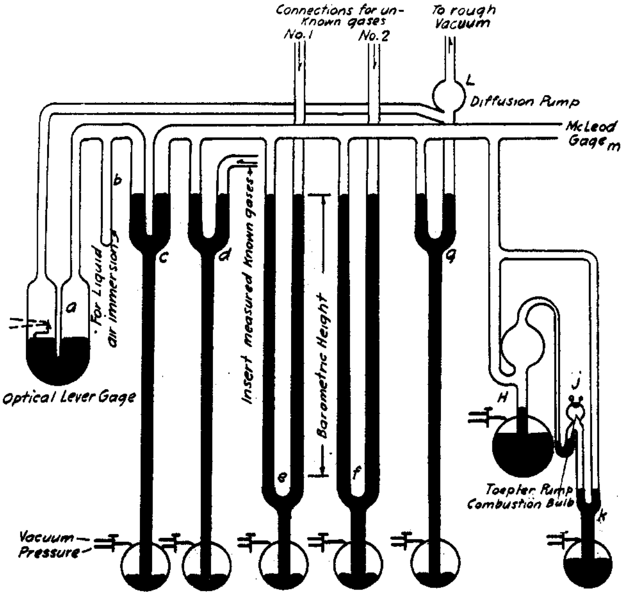

Fig. 1.—Apparatus for the quantitative analysis of very small quantities of gases.

Fig. 1 shows the apparatus for the analysis of gases, and Fig. 2 the apparatus for the generating, purifying and measuring of known quantities of oxygen, hydrogen or carbon monoxide for introduction into the main analysis system.

In Fig. 1 the gas to be analyzed may be introduced through barometric cutoffs *e* or *f* from either of two separate sources. Ex-

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[1] Langmuir, This Journal, 34, 1310 (1912), refers to a method somewhat similar in principle to the one here described.

haustion of the main system takes place at will by opening the mercury cutoff *g*, through which the system is exhausted by means of a mercury diffusion pump *l*. Gases to be added for purposes of combustion are introduced through the mercury cutoff *d*. The freezing out of water vapor and carbon dioxide is accomplished by immersing in liquid air, or solid carbon dioxide, the tube *b*, with the mercury cutoff *c* open. A McLeod gage, *m*, measures the pressures of all gases except water vapor, the pressure of which is measured by means of the optical lever gage *a*. The Toepler pump *h* moves gases from the main system to the combustion bulb *j* for combustion or storage. These gases may be returned to the main system through the mercury cutoff *k*. The combustion bulb *j* contains a small platinum filament for ignition purposes.

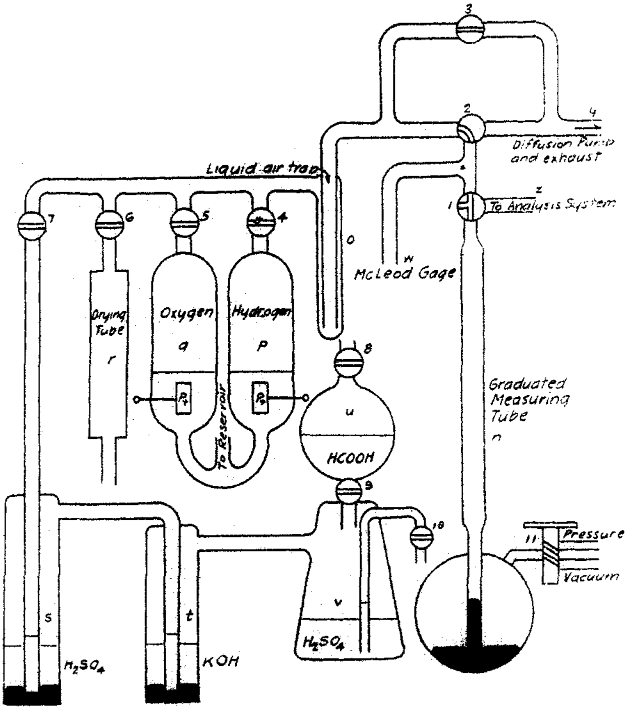

Fig. 2.—Apparatus for the generation and measurement of known gases for use in analysis.

The system for generating and measuring gases, Fig. 2, consists of a manifold into which may be introduced hydrogen or oxygen from the electrolytic generator *p q*; air through the drying tube *r*; or carbon monoxide from the generator *v*, from which it passes through two wash bottles for the removal of carbon dioxide and water. A mercury blowoff valve, not shown, is provided to prevent undue increase of pressure in the carbon monoxide generating system. The manifold is connected through a liquid air trap *o* and stopcocks 2 and 1 to a measuring tube *n*, a rapid reading McLeod gage, *w*, being connected between these stopcocks. Stopcock 2 is so arranged that the measuring tube *n* may be connected to the gas generators or to the exhaust pump *y*, the latter for the complete evacuating of the tube, or for bringing the pressure down to any desired value. Stopcock 1 connects the measuring tube *n* to the main analysis system, or to the gas generating system. Stopcock *3* is provided in a bypass to permit of the evacuation of the system.

In the process of the analysis of an unknown mixture of gases, the following method is used: The system is thoroughly exhausted, using the diffusion pump *l*, and the gas to be analyzed is introduced through a barometric cutoff (*e* or *f*) from the system in which the gas is collected. Liquid air causes the freezing out of carbon dioxide and water vapor in the tube *b*, the other gases being collected in the bulb *j*, using the Toepler pump, after the pressure due to these gases in the system, of known volume, has been determined by the use of the McLeod gage *m*. The carbon dioxide is then released by substituting solid carbon dioxide for the liquid air, bringing the tube *b* to room temperature during the change, and the pressure due to it is measured. After this carbon dioxide is pumped out of the system, the removal of the solid carbon dioxide releases the water vapor, whose pressure is measured on the optical lever gage *a*, the small system *c* to *a* being used. Assuming that combustible gases are in excess, oxygen is added from the system shown in Fig. 2 by letting it pass from the generator *q* into the system, measuring out the desired quantity in the tube *n*, and admitting it to the main analysis system. After its pressure is measured, it is added to the other gases in the bulb *j*, the mixture burned, and the products of the combustion, carbon dioxide and water, separated out and measured as was done before, in the early part of the process. The portion not burned is measured and returned to the bulb *j*. The carbon dioxide formed is a direct measure of the carbon monoxide in the original sample. If the gas to be burned contains no

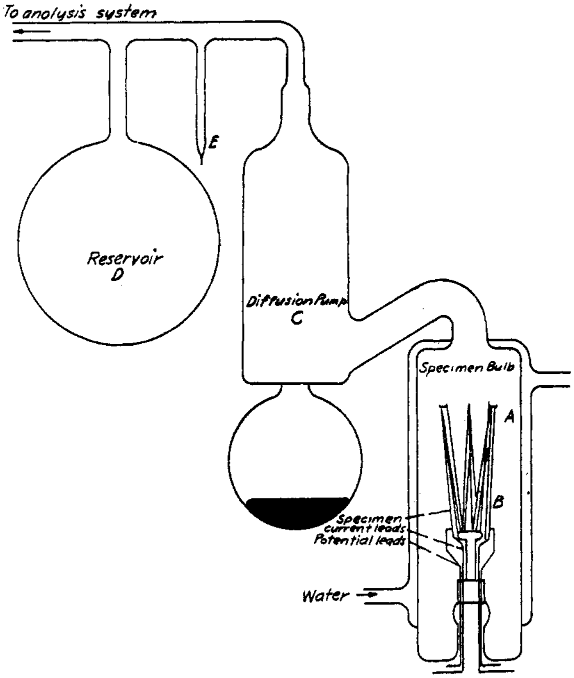

Fig. 3.—System for removing and collecting gases from metals.

nitrogen or oxygen from the original sample, the gas returned to the bulb *j* is the excess oxygen added. A simple calculation determines this point, and if this is found to be the case, the manipulative part of the analysis is completed. If oxygen or nitrogen were present, carbon monoxide is added to the gases in the bulb *j*, as oxygen was, the mixture burned, and the products separated out again. A measure of the gas not burned is sufficient with the data previously obtained, to determine to what extent nitrogen and oxygen were present in the original sample.

The method described above is followed if the gas contains no methane. If methane is present, but no oxygen, the same method is followed, except that much more oxygen is required. If methane and oxygen are both present, complications enter which make the method as described inapplicable without modification.

The following calculations from an actual sample give an idea of the mathematical workings involved:

Gas Analysis Calculations.

Sample of gas taken from silicon steel specimen No. 2, 750 to 800°.

Numbers refer to pressures in the system, in ten thousandths of a millimeter.

H_2O content frozen out and separated.......		= 0		(1)
CO_2 content frozen out and separated.........		= 33.5	3.86 mm³.	(2)
"Dry gases".............................		= 898		(3)
Add O_2...................................		= 535		(4)
Total (dry gases CO_2)......................		= 1433		(5)
Quantity remaining after combustion and freezing out of H_2O and CO_2, res...............		= 605		(6)
Quantity used to form H_2O and CO_2..........		= 828		(7)
One-third of this is O_2......................		= 276		(8)
The remainder was CO and H_2...............		= 552		(9)
CO_2 formed and frozen out..................		= 437	50.3 mm³.	(10)
H_2 burned..................................		= 115	13.22 mm³.	(11)
"Dry gases" from (3)......................		= 898		
H_2 and CO which was taken out (9)..........		= 552		
Remainder to be determined.................		= 346	39.8 mm³.	(12)
O_2 added (4)..........	= 535			
O_2 used (8)...........	= 276			
O_2 left over...........	= 259	259		(13)
New "dry gases" (6)........................		= 605		
Added CO.................................		= 1583		(14)
New mixture..............................		= 2188		(15)
Quantity remaining after combustion and freezing out of CO_2 formed....................		= 1415		(16)
Quantity used to form CO_2..................		= 773		(17)
One-third of this is O_2.....................		= 258		(18)

If no oxygen was present in (12), (18) should check with (13), which is the case. Therefore (12) contains no gas which will burn, which will support combustion, or which will freeze out at temperatures higher than liquid air temperature. This must be nitrogen, or gases from the Helium group.

The analysis is, therefore:

	Mm^3.	Per cent.
CO_2	3.86	3.6
CO	50.30	46.85
H_2	13.22	12.35
N	39.80	37.20

The data sheet for this sample, so far as the analysis is concerned, is as follows:

Sample No. 18.	Feb. 2, 1918.
Dry gases No. 1	898
H_2O content	0
CO_2 content	33.5
O_2 added	535
CO content	437 (CO_2 formed in combustion)
Dry gases No. 2	605
CO added	1583
Dry gases No. 3	1415

If methane is present the calculation is somewhat different, due to the different proportions in the mixture for complete combustion. The same data, however, give complete information for the calculation of the methane, oxygen being absent in the original sample.

In order to determine the accuracy which might be expected from the apparatus described, a number of tests were made toward this end. Hydrogen, oxygen, and carbon monoxide were admitted in varying proportions, each constituent being measured separately as admitted, and then pumped into the combustion bulb. The results of these tests indicate in a very satisfactory manner that the probable error lies well within the maximum allowable, where the total quantity is limited to a few cu. mm., and that much greater accuracy is obtained with somewhat larger quantities.

The following test case, where approximately 65 mm^3. total gases were measured separately and then analyzed as mixtures gives a concrete example:

"As introduced."			Analysis.	
Mm^3.	%.	Gas.	%.	Mm^3.
16	24.8	O_2	23.7	15.5
24.3	36.4	CO	39.9	26.2
25.9	38.7	H_2	36.4	23.8
66.8	..	All	..	65.5

Another analysis shows a maximum error of 6% in the element present, in the greatest quantity, when the total quantity of the sample was less than 5 mm^3.

"As introduced."			Analysis.	
Mm^3.	%.	Gas.	%.	Mm^3.
1.36	28.5	CO	32.2	1.59
2.74	57.3	H_2	51.3	2.54
0.68	14.2	O_2	16.5	0.82
4.78	..	All	..	4.95

These tests, representative of a considerable number, show conclusively the degree of accuracy which may be expected from the apparatus described. Since this accuracy is well within the desirable limits for the class of work for which the apparatus was designed, it has been accepted for such work, and has been in active use for some time with very satisfactory results.

The foregoing gives then, a complete description of an apparatus designed for the quantitative analysis of small quantities of gases, its manipulation, and the results of tests made to determine its accuracy. The gases which can be handled are water vapor, carbon dioxide, carbon monoxide, oxygen, hydrogen, nitrogen, and methane. Inert gases will be classed with nitrogen. The apparatus will handle quantities varying from a few cu. mm., equivalent at atmospheric conditions, to probably one cc., but may be designed for any variation in limits.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE OXIDIZING ACTION OF POTASSIUM DICHROMATE AS COMPARED WITH THAT OF PURE IODINE.[1]

BY CARL R. McCROSKY.

Received September 3, 1918.

The object of this work has been to study some of the analytical reactions of potassium dichromate in an effort to help determine its status as an analytical standard. The time has been devoted, almost entirely to the study of the oxidation of hydriodic acid by the dichromate, the interest in the work being centered, mainly, in the fact that the salt gives a high titration value, *i. e.*, liberates more iodine than its equivalent under the normal conditions of the reaction. Varying these conditions corrects this value in a large degree, yet, it would appear, never wholly corrects it. Our work shows that samples of dichromate from different sources act differently. The experimental evidence we have seems to point to the presence of something in the salt, something to which its

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[1] A thesis submitted to the Department of Chemistry of the Ohio State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.